Review

Formation of Al oxide particles in combustion of aluminized condensed systems

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Abstract

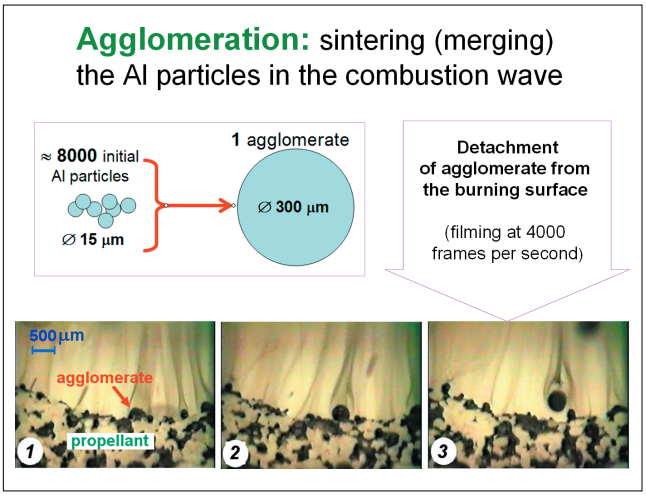
The experimental methods used for characterization of oxide particles formed in combustion of Al containing model solid propellants and pyrotechnic mixtures are briefly discussed. The size distribution and chemical composition of the combustion products are determined using aluminized condensed systems of different formulations burning under atmospheric and elevated pressures. Agglomeration of original Al particles on the propellant burning surface is studied in dependency on the pressure and component composition. The combustion completeness of Al is studied for different propellants and combustion conditions. The burning law of individual Al particles and the fraction of oxide accumulated on the burning particle surface are determined. Recommendations on reducing the Al agglomeration extent are discussed. Formation of nano oxide particles is studied when varying the size of mother Al particle in the range of 10 - 500 micron. The initial nanoparticles compose tens of micron aggregates with fractal-like dimension about 1.6. The aggregates have the electrical charge about few elementary positive or negative electric units.

Keywords : combustion, aluminum, agglomeration, oxide, spherules.

1. Introduction

Using the metal as an efficient rocket propellant fuel has been suggested in the eve of the rocket era by Russian pioneer of space exploration Yu. Kondraryuk[1]. The practical realization of this idea started in USA and USSR in 1960[2),3)]. Unfortunately, the high effectiveness of metalized solid propellant could not be totally realised in practice due to the metal agglomeration, which is characterised by essential enlargement of initial aluminium particles size in the combustion wave. This may lead to formation of slag in the rocket motor and incompletion of metal consumption. Initial efforts to study combustion mechanism of Al particles were undertaken in 1960 - 1970. The state-of-the-art of the researches in the field of agglomeration studies in 1980 - 2000 has been presented in several reviews[4)-7)], which state that the metal agglomeration depends both on propellant formulation and combustion conditions. Actually, the following two characteristic features of the combustion of aluminized propellants determine their total efficiency in solid rocket motors : (1) the agglomeration phenomenon, and (2) the conversion of metal into oxide accompanied with formation of condensed combustion products. Figure 1 illustrates those features.

As is seen in Figure 1, detached from the propellant surface agglomerates burn in two-phase flow of combustion products generating various size oxide particles. Condensed combustion products (CCP) consist of coarse agglomerate residues containing oxide and non-consumed metallic aluminum, as well as of relatively "coarse" oxide particles, which formed after full burnout of agglomerates or original Al particles, and oxide fine smoke particles composed of nanosized spherules. Despite relatively long history of exploiting metalized solid propellants the mechanism of agglomeration is still not known in detail and performance of any new propellant formulation takes individual study. The parameters of CCP determine not only completeness of chemical energy release but also the values of two-phase losses of specific impulse and mass of slag in the combustion chamber, the effect of the nozzle erosion, the optical characteristics of plume and ecological impact of the rocket motor operation on environment. Thus, there exists strong need to know proper CCP parameters. In the present paper, we



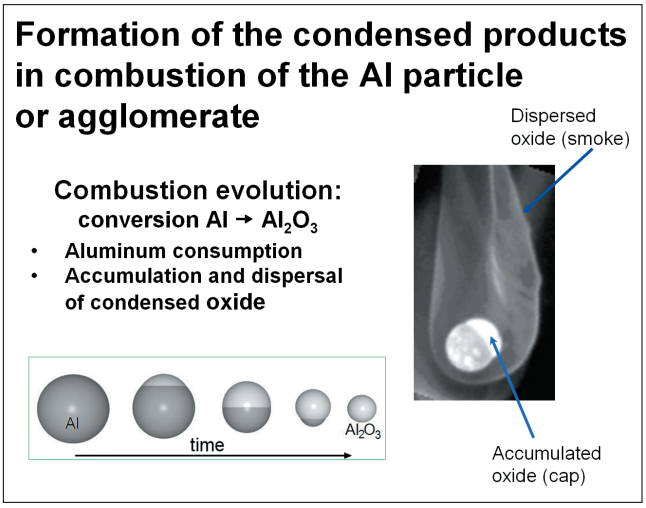


Figure 1 Agglomeration and formation of condensed combustion products are characteristic features of aluminized propellants combustion.

generalized the experimental results on agglomeration characteristics, the mechanism of agglomerate and individual Al particles combustion, aluminum oxide particles formation. Reported results were obtained by authors with coworkers in Novosibirsk in 1990 - 2010.

2. Common properties of CCP

Typical mass size distribution function of CCP is schematically shown in Figure 2.

It has been found experimentally[8)-12)] that the size distribution function has several modes. The "global" mode 1, with maximum in the range of D = 0.3 - 2 micron, is usually associated with the condensation of oxide vapors on nucleation centers followed by coalescence of produced primary oxide particles in the vicinity of burning mother particle. The formation of the micron-size oxide particles, forming mode 2, is assumed[13)] to be a result of transformation of oxide cup, presented on each burning particle during combustion, into single oxide particle after total consumption of aluminum. The size distribution of such oxide particles depends on the size distribution of burning Al-particles (both agglomerates and non-agglomerated particles). It was established a correlation between the mother and the final oxide particle diameter.

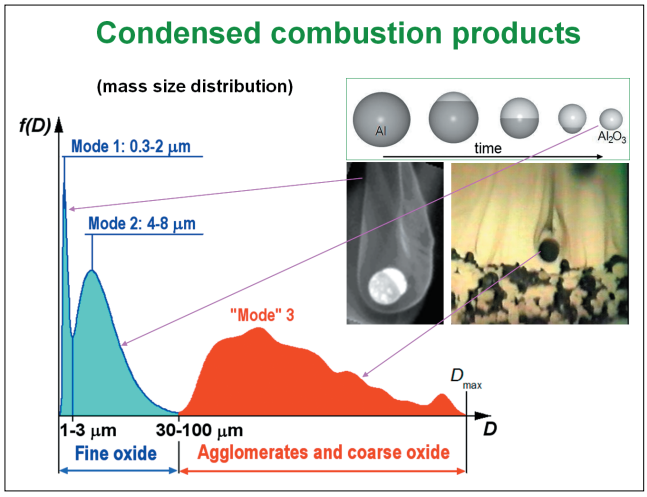


Figure 2 Multimodal character of the CCP size distribution function.

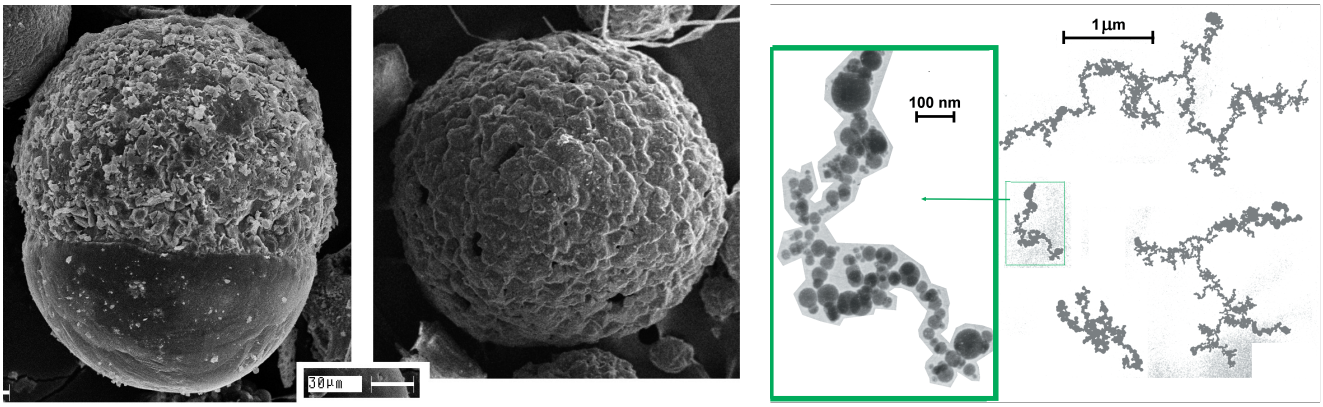
In the simplest case, if the mass fraction of non-agglomerated Al particles is large enough, the mode 2 size range can be attributed directly to the original size distribution of aluminum particles in the propellant. For example, the mode 2 with size of ≈4 micron was recorded in the case when we used commercial Al powder ASD-4 with characteristic size about 5-6 micron[13)] and when essential part of Al particles ejected from the burning surface without agglomeration. Finally, the global mode 3 stands for agglomerates consisting of aluminum and aluminum oxide; the term "mode" here is rather conventional since the size distribution of agglomerates can be multimodal itself.

3. Experimental techniques and main results

In general, the CCP size distribution function is extremely complex and wide, see Figure 3.

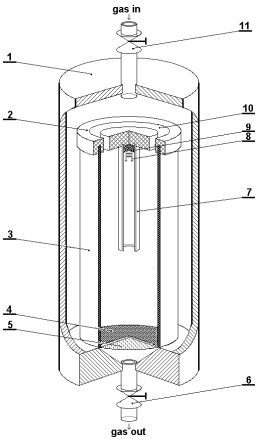
It comprises 8 orders of magnitude in abscissa (diameter), namely, from 10^{-10} m to 10^{-2} m, and ca. 6 orders in ordinate (relative mass density distribution). Therefore the investigation of CCP is difficult technical problem. The intrusive instrumental (so called contact) methods have been widely used to obtain valuable experimental information[14)]. Such methods include the technique for quenching and collecting the particles and techniques for subsequent analyses of particles to determine their size distribution, chemical composition and other required characteristics. The manifold contacts methods and their problems and difficulties are discussed in [15)]. We developed original experimental technique[8), 13)] based on using special design flow through bomb (working pressure up to 150 atm), Figure 4, supplemented with specific methods for particle size and chemical analyses[16)-17)].

The quenching of the burning Al particles is performed via mixing with co-current flow of inert gas at given distance from the burning surface; up to 20 cm depending on the length of protective tube. Then the particles are trapped with the metal grids and aerosol filter. The key features of the method are: practically no limits in the size of sampled particles, short time interval between quenching and sampling (0.1 - 40), and the possibility to



a b c

Figure 3 Different size CCP particles: a) - acorn shaped agglomerate of 300 micron size quenched at the early stage of the combustion (unburned Al is on the bottom, oxide cup on the top); b) - same size agglomerate quenched at the final stage of the combustion, totally consisted of oxide; c) - micron-sized fractal aggregates composed of spherules - primary nano-sized oxide particles.



1 – bomb body,
2 – top cover of the cylinder3,
3 – thin wall cylinder,
4 – stack of wire mesh screens,
5 – Petrianov aerosol filter AFA type,
6 – gas outlet valve,
7 – protective tube,
8 – ignition wire,
9 – propellant specimen,
10 – ring slot for blowing the cylinder3,
11 – gas inlet valve.

Figure 4 Chart of the bomb for CCP sampling.

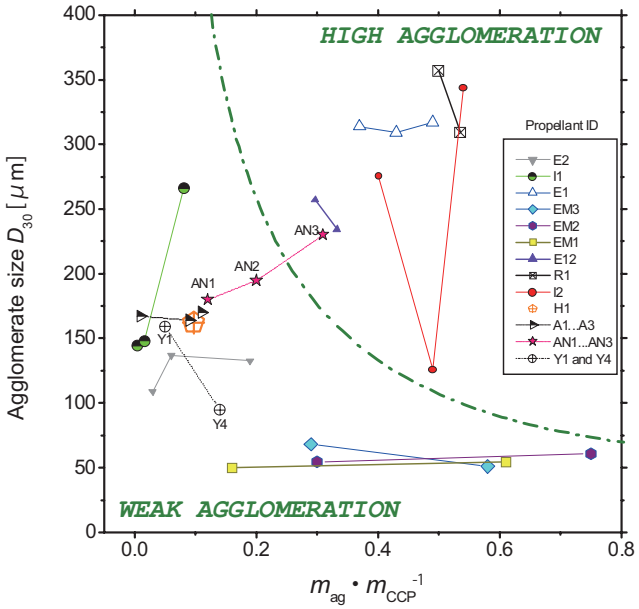


Figure 5 Map of Al agglomeration trends.

investigate the burning particle evolution (in terms of size, morphology and chemical composition) via varying the quench distance. When experimenting in a flow through bomb, we analyzed the oxide and agglomerate particles in the range from 0.5 micron to maximal size (up to few millimeters). The effects of the wide set of the formulation factors on CCP parameters were systematically investigated. In particular, the agglomeration process and the aluminum combustion efficiency were characterized at pressures 40-60 atm in terms of the size distribution function and unburned aluminum content. The effects of the following factors have been studied: (1) the nature of binder - inert *vs* energetic; (2) the nature of components and their combination - AP *vs* nitramine RDX, HMX, CL-20; (3) the modification of metal fuel - use of polymer-coated Al, addition of nano-sized Al, replacement of Al by Al/Mg or Al/B alloys. The results of these studies show that unburned aluminum content in agglomerates and their size distribution (as well as the sizes of oxide particles) is controlled by not only geometrical structure of propellant and burning rate, but also the listed formulation factors, see[10)-13), 18)-21)] for details. Some generalization of the experimental results is presented in Figure 5 in the form of diagram showing the high and weak agglomeration trends for studied model propellants. High agglomeration trend is characterized by the location of the point, represented the propellant under study, in the upper right corner of diagram (large value of agglomerate size D_{30} and large mass fraction of agglomerates in CCP m_{ag}/m_{CCP}). Accordingly, the left lower corner in diagram corresponds to the weak agglomeration trend. The summary of these results is presented in Table1.

Note the trend for most typical formulations: the greater agglomerate size, the bigger content of unburned Al in agglomerates.

In addition, the 100 - 500 micron Al particle and Al agglomerate combustion evolution in the combustion products of a model solid propellant have been investigated in via use of novel approach[22)-24)] based on experimenting with specially designed specimens generating mono-disperse burning particles. For 470 and 340 micron agglomerates the empirical dependencies of the incompleteness of aluminum combustion on time t and pressure p were determined. It was shown that for fixed p and t, agglomerates of small size reach the higher degree

Table 1 Characteristic parameters of agglomeration trends and types of propellant formulation[13].

No	Propellant ID	HIGH AGGLOMERATION TREND m_{ag}/m_{CCP}=0.3÷0.54, D_{30}=130÷430 μm	Nitramine
1	I2	isoprene rubber + catalyst	-
2	E1, E12, AN3	buradiene-nitryl rubber +DEGDN	HMX
3	R1	buradiene-nitryl rubber +DEGDN	RDX
		WEAK AGGLOMERATION TREND m_{ag}/m_{CCP}=0.01÷0.20, D_{30}=140÷270 μm	Nitramine
4	E2	buradiene-nitryl rubber +DEGDN	-
5	I1	buradiene rubber	HMX
6	AN2	buradiene-nitryl rubber +DEGDN, Alex	HMX
7	H1	HTPB	-
8	Y1, Y4	polyvinyl tetrazole polymer + nitroester	HMX
		High-burning-rate propellants (r_b>40 mm/s at P=4MPa) m_{ag}/m_{CCP}=0.01÷0.30, D_{30}=50÷230 μm	Nitramine
9	EM1	isoprene rubber + ultrafine AP	HMX
10	EM2, EM3	isoprene rubber + ultrafine AP	-
11	AN1	buradiene-nitryl rubber +DEGDN, Alex	HMX
12	A1, A2, A3	buradiene-nitryl rubber +DEGDN, Alex	-

of conversion than the agglomerates of larger size. For the burning 100 micron mother particles the size, density, and morphology of the final oxide particles were studied for the first time. It was found that the mass fraction of the final oxide particles is approximately 0.2 of the initial value of mother particle mass. After completion of the combustion, the mass fraction of oxide deposited on a particle is ≈0.1 of the mass of the entire oxide formed and it does not depend on the pressure in the investigated pressure range 7 - 80 atm. The ratio of the masses of the accumulated and removed oxide is determined primarily by the size of the burning particle. The smaller the particle, the less oxide fraction which is deposited on the particle and the more oxide mass is carried away into the external gas flow.

The way to reduce the Al agglomeration can be proposed consisting of two steps. At the first (theoretical) step one has to conduct preliminary thermodynamic calculations with variation of the propellant components and compositions to reach high completeness of aluminum combustion and high specific impulse. At the second (experimental) step (see Figure 6) one should vary the particle size distribution and Al particles properties in order to reduce agglomeration and provide needed level of the burning rate. The step 2 can be repeated in a cyclic manner by means of changing the propellant formulation after examination of the condensed combustion products characteristics.

The study of nanosized oxide particles formation allowed obtaining information on size distribution function of primary spherical particles - spherules, on concentration, structure (including the fractal-like dimension) and size distribution of aggregates composed of spherules, on the electric charge of aggregates, etc. The

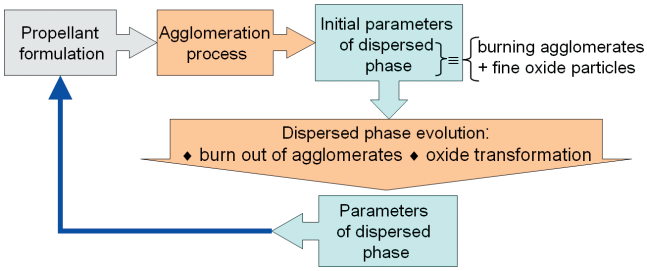


Figure 6 Proposed scheme of propellant optimization via studying CCP.

experimental techniques and the results are reported in original works[25)-33)]. The main findings are: the alumina nanoparticles initially form the chain-branched shape aggregates with fractal dimension of about 1.6. Aggregates are composed of spherules of 10 - 140 nm in diameter. The outer gabarite size of aggregates varies in the range from 0.1 to few microns. The majority of the aggregates are charged either positively or negatively. The typical value of charge of aggregates is a few elementary units. Some of the aggregates are dipoles. The Coulomb interaction plays important role in the processes of clasterization and coagulation and is responsible for determined reduced value of the fractal dimension (1.6 instead of 1.8, the latter corresponds to Brownian diffusion mechanism). The size distribution of alumina spherules depends on the size of the burning mother particle[32),33)]. In particular, the mean diameter of spherules increases from ≈17 nm to ≈68 nm when burning particle diameter increases from 4 to 340 micron.

4. Conclusions

The considerable progress has been achieved in the development of the experimental techniques designed for

investigating the CCP particles characteristics. As a result, numerous data on the dependencies of the CCP particle size distribution and completeness of metal combustion on the propellant formulation and combustion conditions has been obtained. The great efforts have been also undertaken in theoretical studies. The modern tendency in theoretical modeling of agglomeration is the use of realistic packing of particles, see, for example[34]. However, the new models are basically similar to the pocket models developed by Grigoriev, Zarko[35] and Cohen[36] many years ago. Contemporary models still do not allow predicting a priori the agglomerate size distribution function and completeness of aluminum combustion because the models can not describe in detail the processes in condensed phase. The reason is the lack of accumulated data on physics and chemistry of the processes in the surface layer of burning propellant. The further progress is expected on the road of experimenting with well characterized mixtures (including some novel ingredients) and using advanced experimental techniques like high heating rate calorimetry, high speed video recording, etc. This may lead to understanding the processes on a particle-size scale level and facilitate development of detailed physicochemical agglomeration models.

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